USAFOEHL REPORT

86-058EO0058HTB

ASSESSMENT OF CS ENVIRONMENTAL TOXICITY AT EGLIN AFB FL

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August 1986

Final Report

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UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

AD-A171685

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY NA	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution is unlimited.
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE NA	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) USAFOEHL Report 86-058E00058HTB	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION USAF Occupational and Environmental Health Laboratory 6b. OFFICE SYMBOL (If applicable) ECO	7a. NAME OF MONITORING ORGANIZATION
6c. ADDRESS (City, State, and ZIP Code) Brooks AFB TX 78235-5501	7b. ADDRESS (City, State, and ZIP Code)
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Same as 6a 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)

Assessment of CS Environmental Toxicity at Eglin AFB FL

12. PERSONAL AUTHOR(S)
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13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Final	FROM ____ TO ____	August 1986	35

16. SUPPLEMENTARY NOTATION

N/A

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	o-chlorobenzylidene malononitrile CS environmental toxicity environmental fate CS environmental degradation

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

This report was written in response to a request from Eglin AFB. It provides a hazard assessment and recommendations regarding the environmental toxicity of CS in soil resulting from use of CS in training exercises at Eglin. The hazard assessment was developed in two parts: (1) A simplified model of the degradation of CS deposited in soil was developed based on the monoexponential equation $A_C = A_0 e^{-kt}$. This allowed an estimated $t_{\frac{1}{2}}$ of 3.9 days to be determined for CS in Eglin soil. (2) A comprehensive interpretive review of CS literature was performed with the goal of developing a coherent picture of CS environmental toxicity. Recommendations for use of CS at Eglin AFB were developed by integrating the information obtained from the literature review and the model of CS soil degradation. Recommendations were that CS could be used at Eglin and that the soil burden would depend on the deposition rate from training exercises. Management of CS use should include rotating exercises. Management of CS use should include rotating heavy-use CS training sites, to avoid buildup of CS at any single site and avoiding heavy use at sites which drain directly

(over)

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS	Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL
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DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

UNCLASSIFIED

Item 19, cont'd.

into areas where aquatic species may be exposed. A comprehensive CS bibliography is also included.

Acknowledgment

The authors wish to acknowledge the invaluable assistance of 1Lt J. Muilenburg, Maj T. Doane and Lt Col M. Anderson in completion of the field study of CS degradation and preparation of this report.

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I. INTRODUCTION

A. Purpose

This report was prepared at the request of USAF Regional Hospital Eglin/SGPB. It provides a review of o-Chlorobenzylidene Malononitrile (CS) environmental toxicity and specific information concerning the degradation rate of CS on Eglin soil. In addition, it contains recommendations concerning the use of CS and addresses the issue of environmental effects associated with field use of CS in training exercises at Eglin AFB. It also contains a comprehensive bibliography which provides an overview of CS information.

B. Problem

Eglin AFB is experiencing an increase in use of CS. Use of CS in field training exercises ultimately leads to some degree of soil contamination of the training site by CS and its degradation products. General environmental concerns regarding CS soil contamination at Eglin can be appropriately clarified and focused by addressing component issues such as:

Is CS degradable in the environment and how quickly?

What is the dose-effect relationship between environmentally dispersed CS and potential toxic effects?

The answers to these questions can then be used to address other pertinent Eglin CS issues:

Increased restrictions/limitations on use of CS

Requirement for possible alternate agents

C. Scope

The scope of this report is broad. The CS environmental toxicology review is specific to Eglin AFB. However, the concepts may be used by other installations faced with similar decisions. The CS soil degradation study was conducted using Eglin soil and is therefore specific to Eglin. However, the technique used to determine CS soil degradation rate is straightforward, and our validation allows it to be used to study soil from other bases for similar determinations. In addition, validation of an analytical method for CS soil assays will allow USAFOEHL to support a requirement for CS soil analysis. Finally, the bibliography on CS will provide others interested in CS a comprehensive list of the available CS literature.

II. DISCUSSION

A. CS Soil Degradation Study

1. Background:

The extent of CS soil contamination in soil at Eglin AFB is dependent upon two factors: The extent of CS dispersion, (the frequency and

extent of field exercises) and the degradation rate of CS on soil. An estimate of the extent of CS deposition via field exercises which can be tolerated in soil can be made by determining the CS degradation rate on soil. Because of the dependence of CS degradation on soil factors, it was necessary to perform CS degradation studies using typical uncontaminated, Eglin soil. Because Eglin soil is primarily fine sand with a small amount of humus material, it is likely that limited soil binding and hydrolysis occur. Hydrolysis may increase with rain or mist contact with the CS-contaminated soil. In addition to determining the CS degradation rate we also assessed the effect of several variables on this rate; including light, added moisture, and multiple exposures of CS onto the same soil over an extended period. We did not analyze for CS degradation products; however, we evaluated some samples for extent of CS aerosolization.

2. Materials and Methods:

Typical uncontaminated soil was obtained from Eglin AFB. Soil was shipped and stored in clean one pound coffee cans covered with aluminum foil and plastic tops. The soil was slightly moist, but due to its high sand content was readily screened. Capsulated CS IAW T.O. 11C5-5-2-7 was obtained from the USAF School of Aerospace Medicine, Education Division, Battlefield Medicine Operations Branch, Brooks AFB TX. After determining the CS purity, it was thoroughly mixed with silica gel to produce a 1% CS mixture for soil application. Recovery of CS from this silica mixture was >99%. Use of this silica-CS mixture improved handling qualities of the CS.

CS was applied to soil in the following manner: Fifty grams of soil was measured into a shallow plastic dish. The soil was spread evenly across the bottom of the dish. The soil depth was approximately 0.5 cm and the surface area was approximately 95 cm^2. The dishes were allowed to sit for several hours to allow normal loss of surface moisture. Following this stabilization period 1.0 gm of the 1% CS-silica mixture was distributed evenly over the soil surface by gently pouring from a weighing boat (yielding a concentration of 200 ppm CS in soil by weight and an approximate surface concentration of .11 mg/cm^2). The soil was then placed into a Warren Sherer CEL44 environmental chamber.

The environmental chamber provided 16 hours light and eight hours dark/24 hours. Light intensity was approximately 1600 foot candles in the environmental chamber. The chamber maintained a temperature of 80°F during the light phase and 50°F during the dark phase. Humidity was held at 45± 10%. The CS contaminated soil was removed in replicates of five at appropriate time intervals from 12 hours to 28 days (the 12 hour replicates received continual light while all others received the 16/8 regimen). Due to a malfunction in the environmental chamber refrigeration unit on days 13-18, temperatures ranged between 80° to 92°F. The humidity also dropped to 30% during this period.

The effects of selected variables were also tested. The effect of light on CS degradation rate was examined by covering two sets of five replicates in the environmental chamber with aluminum foil to prevent light exposure. These replicates were removed and analyzed at 2 days and 7 days.

The effect of moisture on CS degradation was tested by spraying the CS containing soil samples with water. Distilled water was applied using a spray bottle which delivered .15 mL/pump. One replicate received 0.9 mL on days 1, 2, and 3 while the other received 9.0 mL on day 1. Both replicates were analyzed for CS content on day 4. The extent of aerosolization was evaluated by placing replicates into sealed "zip loc" bags within the environmental chamber. Both soil and "inner bag surface" were analyzed for CS content after 4 days. The effect of multiple CS applications on soil CS level was evaluated by applying CS (1.0 gm of 1% CS-silica mixture) on days 0, 2, 4, 6, and 8. Replicates were analyzed for CS content on day 10.

The CS content of soil samples was determined in the following manner: The soil sample was extracted with methylene chloride for one hour with occasional gentle agitation. In the case of the "zip loc" bag the inner surface was rinsed with methylene chloride to remove CS. Following extraction, an aliquot of the extract was pressure-filtered through a glass-fiber filter. Final cleanup was accomplished by passing the extract through a 4 µm filter. Following cleanup, 5° µL of extract was injected into a Hewlett Packard 1084B liquid chromatograph under the following conditions:

Mobil phase: methanol/H_2O (50:50) at a rate of 1 mL/min
Column: 5 µm LCPAH
25 cm x 4.6 mm, Supelco Inc.
Detector: Variable wavelength UV, 305 nm

An external standard was prepared by dissolving CS in methylene chloride and analyzed along with the samples. Quantitative sensitivity of 2 ppm CS in soil was achieved using this method.

3. Results:

The amount of CS in the soil samples decreased exponentially with time. The decrease can be approximated by the monoexponential equation:

$$A_o = A_e^{-kt}$$

At 28 days <1% of the original CS remained. CS had a half-life ($t_{1/2}$) of 3.9 days on the soil under the conditions specified (Appendix A, Figure 2). Added moisture resulted in increased degradation of CS, while holding CS under light-free conditions resulted in reduced CS breakdown (Appendix A, Table 2). CS was found to accumulate on soil when multiple 48 hour-interval applications were made to soil replicates; however, we were unable to accurately determine the extent of CS aerosolization due to unexpected increased loss of CS within the "zip loc" bagged soil samples (Appendix A, Table 2). The amount of CS lost in four days within the bags was 78% vs 49% for open soil replicates, while only a trace amount of CS was found to be adhered to the inner surface of the bags.

4. Comments:

Our study models one component of the process of CS environmental chemicodynamics (the quantitative assessment of the fate of chemicals in the

environment). It should not be confused with the more complex and ambitious complete modeling of environmental chemicodynamics of CS. However, because most concerns at Eglin were centered around CS exposure related to surface contact, and since we confirmed that CS has a short to moderate environmental $t_{1/2}$ (3.9 days), we believe our simplified approach is adequate. CS degradation is impacted by environmental factors. Simulated rainfall or mist increased CS degradation (Appendix A, Table 1) when compared to control soil replicates which did not receive moisture (35% vs 51%). However, there was no difference in the effects of multiple application of small amounts of water (mist) versus one large amount of water (rain). In addition, soil replicates which received no light showed a reduced rate of CS degradation. Since our light intensity was much less (about 1/3) than that for normal field conditions, this factor would be even greater under field conditions.

The 22% CS recovery from soil samples maintained in "zip loc" bags for four days is surprising (open soil recovery was 51%), particularly since only a trace of CS was found on the inside walls of the bags. This compares with a 98% recovery from soil and 2% recovery from the inside bag surface for soil replicates held only about five minutes in "zip loc" bags. This 2% appears to have been drawn almost immediately from the soil surface, along with the silica carrier, to the bag surface by electrostatic forces.

Since there was little CS detected adhering to the inner surface of the bags we can only assume that an enhanced CS degradation occurred in the closed environment of the bags. Although the mechanism for this degradation is unclear, it does demonstrate that CS degradation is significantly affected by environmental factors. In addition, our failure to detect significant amounts of CS adhered to the inner surface of the "zip loc" bags, along with CS's very low vapor pressure suggests that aerosolization was not a significant factor in CS loss from our soil samples. Nevertheless the odor of CS could be slightly detected in the environmental chamber after several weeks of use, indicating some aerosolization had taken place, possibly from movement of the soil containers.

Because our conditions were rather moderate compared to actual Eglin field conditions, we believe our estimated soil $t_{1/2}$ is conservative. Other environmental factors that may increase the degradation of CS in the field as compared to our laboratory study are: temperature extremes, wind-aided aerosolization, and transfer of CS to subsurface soil via rain. Thus, the actual loss of CS from the soil surface under field conditions at Eglin should be more rapid than our estimated 3.9 days. Based on the monoexponential degradation rate estimated for CS we can calculate the mean accumulation of CS on surface soil at equilibrium (achieved after five to six $t_{1/2}$'s following multiple equal applications of CS) using the following equation:

$$\frac{1.44 \times t_{1/2}}{\text{application interval}} = \text{mean CS accumulation}$$

(Principles and Methods of Toxicology, Hayes, 1984)

Our estimated $t_{1/2}$ of 3.9 days and application interval of 2 days can be used to calculate an estimated mean accumulation of 2.8 times the amount of CS applied at each interval. This is in good agreement with the

accumulation of CS found in the soil replicates (Appendix A, Table 1) which received five CS applications at two day intervals and were analyzed two days after the fifth application (2.7 times the amount applied at each interval). Thus, we have estimated a degradation rate with $t_{1/2}$ of 3.9 days for CS, and confirmed the accuracy of our estimate using multiple soil applications of CS, to produce an accumulation of CS which closely approximates our predicted accumulation using a monoexponential degradation scheme and estimated $t_{1/2}$. Peak levels of CS (encountered immediately following field exercises) would, of course, be somewhat higher than the mean accumulated CS value. Nevertheless by examining the effect of various intervals for field exercises in which similar amounts of CS are dispersed to the soil, predictions can be made regarding levels of CS which will accumulate in the soil. For instance, field exercises in which CS was dispersed at 3 day intervals for 3 weeks would result in soil accumulation roughly twice the amount dispersed the first day, during the last few days of the 3 week period. A less intense use of CS involving dispersion at 7 day intervals would result in mean CS soil accumulations slightly less than that dispensed at each exercise. Thus, we can reach several useful conclusions from our soil degradation study:

- Multiple dispersions of CS in one area may result in an accumulation of CS. The extent of accumulation will depend on the amount of CS dispersed and the dispersion interval.

- Regardless of what CS level occurs in Eglin soil following exercises, within 3 to 4 days it will be reduced to 50% of peak levels.

- Three to four weeks following a CS dispersion only about 1% of the original CS should remain.

- Rainfall or heavy dew will increase the breakdown of CS.

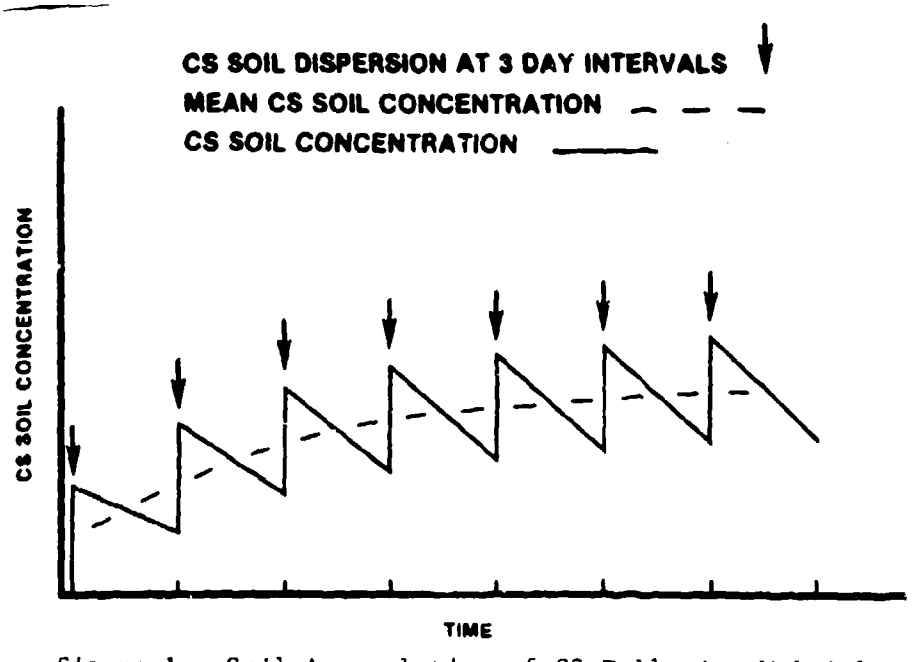

Figure 1: Soil Accumulation of CS Following Multiple Applications

B. Review of CS Toxicology

1. General Aspects:

CS is a white crystalline solid with the odor of pepper. It was initially synthesized in 1928 by Corson and Stroughton who noted its extremely irritating properties. These properties led to its introduction in 1958 as a riot control agent. It is also used by the military for terrain denial and training purposes. It is disseminated as an aerosol by burning, by micropulverized powder dispersion, or as a methylene chloride or acetone solution.

2. Environmental Fate of CS:

The most significant degradation mechanism for CS in the natural environment is hydrolysis (Appendix B). CS is only slightly soluble in water (2-3%) but will slowly hydrolyze to form o-chlorobenzaldehyde and malononitrile. The half-life of CS in an aqueous medium at 25°C is 2 days (Vojvodic). The persistence of CS in soil is dependent upon climate weather, and CS formulation. Treatment of CS with prolonging agents such as silicone can greatly increase environmental persistence. CS at a contamination density of 11 gm/m^2 on soil may persist in excess of three months (Sansonetti). CS from a grenade has been found 30 days following detonation over snow, 70 yards downwind (Johnsen and Blanch). The rate of CS hydrolysis will also depend on local soil factors such as pH and soil moisture content. Hydrolysis is expected to proceed rapidly in an alkaline environment.

Other hydrolysis products of CS are o-chlorobenzoic acid, a product of o-chlorobenzaldehyde; and linear malononitrile dimer, and cyclic malononitrile dimer, products of malononitrile. From the breakdown scheme (Appendix B) it is apparent that o-chlorobenzoic acid is the principal stable breakdown product. Thus, while initial environmental concerns from a single CS dispersion might be for CS, o-chlorobenzaldehyde, and malononitrile effects, these chemicals would hydrolize with time to more stable (and less toxic) products.

3. Toxicity of CS:

Short-term exposure: A significant amount of information is available regarding short-term exposure to CS. It is a potent lacrimator, respiratory and skin irritant. Sensitivity to eye, respiratory, and skin effects of CS has considerable individual variability. Skin irritation occurs at levels of 10 mg applied for one hour. Moisture on skin enhances CS toxicity. The threshold for eye irritation is 4 $\mu g/m^3$ (Beswick), while an effective concentration is considered to be 5 mg/m^3. The reader is referred to the bibliography (Appendix C) for references that address short-term exposure. OSHA has recommended an Immediately Dangerous to Life and Health Level (IDLH) of 2 mg/m^3 and a PEL of .4 mg/m^3. Although short-term effects are of paramount importance for military uses of CS, the issue of environmental toxicity transcends short-term concerns and requires evaluation of such issues as chronic toxicity, mutagenicity, teratogenicity, immunotoxicity, and ecotoxicity.

CS mutagenesis and teratogenesis: CS is a potential alkylating agent. Concern for its mutagenic potential has stimulated a number of researchers to investigate the mutagenic capability of CS in in vitro systems. CS has been tested in a number of short-term mutagenicity assays including the Ames test, mouse micronucleus test, sex-linked recessive lethal mutation test in Drosophilae (Wild et al.) and mouse lymphoma test (National Toxicology Program). Only the mouse lymphoma assay was positive. When pregnant rats and rabbits were exposed to CS there were no indications of teratogenicity or embryolethality (Upshall).

Chronic toxicity and carcinogenesis: CS has shown no capability to accumulate within exposed animals. The CS $t_{\frac{1}{2}}$ in blood is extremely short (Leadbeater, 73). A chronic inhalation study by Marrs et al. found no increase in tumors in three species of laboratory animals. CS has also been included in the National Toxicology Carcinogenesis Testing program. Histopathologic evaluation of tissues from this study has been completed, but the study must be reviewed prior to release. Results should be available in 1987.

Immunotoxicity and endocrine toxicity: CS has been reported to have some skin sensitizing potential following occupational exposure (Schmunes and Taylor, Levin and Mershon). Studies in laboratory animals also suggest some suppression of humoral immunity (Nagarkatti et al.). In addition, researchers have reported CS effects on the thyroid, adrenal, and seminiferous tubules in laboratory animals (Chowdury et al.).

4. Toxicity of CS Breakdown Products:

CS degrades via hydrolysis to a number of products (Appendix B). However, most are of slight significance because they degrade quickly to other products, or only occur to a minor extent. Those products which are of concern because of extent of occurrence or toxicity are: o-chlorobenzoic acid, malononitrile, and to a lesser extent malononitrile dimer. Malononitrile is the most toxic of CS hydrolysis products. With an oral LD_{50} of less than 100 mg/kg in rodents it is classified as very toxic. Its toxicity is similar to cyanide and some investigators have suggested that metabolism to cyanide may be the mechanism involved in malononitrile toxicity (Willhite and Smith). Malononitrile is also a skin and eye irritant. A product of malononitrile, malononitrile dimer (1, 1, 3-tricyano-2-amino-1-propene) was initially identified as a contaminant in an aqueous solution of malononitrile, however, its toxicity has not been extensively studied. Two unique properties are known about this compound. One is its unusual ability to stimulate RNA synthesis in the brain. The other, more recently reported property, is its antithyroid effect (Dhindsa). O-Chlorobenzoic acid is a significant detoxification step in the hydrolysis of CS. It has an oral LD_{50} in rodents of greater than 6 gms/kg. However, it is moderately irritating to the skin and highly irritating to eyes. Thus, hydrolysis of CS produces both malononitrile, a more toxic but less stable product; and o-chlorobenzoic acid, a less toxic and more stable product. Both products have some skin/eye irritant potential.

5. Ecotoxicity:

Reports of CS environmental persistence (Sansonetti et al. and Johnsen and Blanch) have raised concerns about the impact of CS used in field exercises on natural species which inhabit the area. A number of reports are available concerning the potential ecological effects of CS. The effects of CS on both aquatic and terrestrial vegetation have been evaluated (Worthley and Schott and Morrison, et al.). The principal aquatic plant species used in CS studies was the duckweed. The growth of two of the three duckweed species tested was reduced at a CS concentration of 1 ppm, while all three had reduced growth at 5 ppm. The hydrolysis products of CS were also tested for toxicity. It was determined that acute toxicity of CS to aquatic plants is probably due to its breakdown product, malononitrile. CS has been tested on both woody and herbaceous terrestrial plants (Morrison et al.). The effects of CS on plants appears to be principally due to contact damage. Woody and herbaceous species both showed a wide variability of leaf damage and reduction in shoot growth. Doses used in terrain denial type situations (60-120 gm/m^3) caused significant leaf damage. The effects of soil incorporated CS also varied with species, but in most species some reduction of seedling emergence occurred when CS was applied within 4 weeks of planting. Tests of plants at the incapacitating level for personnel (10-20 mg/m^3) did not cause appreciable plant damage.

The aquatic toxicity of CS has been reported in two species of fish, the rainbow trout and the mumichog. The trout had toxicity at levels of 0.1 mg/L, while the mumichog, a species more like that found at Eglin, had a lethal threshold concentration of 3.9 mg/L. It is thought that aquatic CS toxicity is principally due to malononitrile, its hydrolysis product.

The toxicity of CS to wildlife has not been extensively studied, however, numerous reports on toxicity to laboratory animals are available. In addition, McNamara has reported acute toxicity studies on some domestic species. A threshold lethal concentration of 1806 mg/m^3 for 10 minutes has been reported for the rabbit, while an acute oral LD_{50} of 400 mg/kg has been reported (lower values have also been reported). A thirty day feeding study was done in both rabbits and rats. A decreased weight gain was reported for the high dose group of rabbits (500 mg/kg estimated dose based on food consumption). It appeared that some tolerance to oral CS developed during the course of the study. The repellancy of CS-contaminated seeds for Deer mice and House mice has been evaluated (Schafer and Bowles). Seeds were treated with 1-2% of the chemical. CS, along with numerous other chemicals, was found to markedly decrease intake of treated seeds.

6. Comparison of Tear Gas Agent Hazard

A number of compounds have been proposed or used as riot control agents. Riot control properties also cause these agents to be considered by the military for terrain denial and training purposes. Most of the agents are solids and dispersed as fine particulate smoke or aerosols. Appendix D provides a summary of the effects of the more important agents. These agents can be divided into two groups; lacrimators, that act primarily on the eyes to cause pain/irritation and tearing, and sternuators, which act principally on

the upper respiratory tract to produce sneezing. There is an overlap of effects between the two groups and both cause nausea and vomiting at high exposures. According to Sim a property which limits use of sternuators for training purposes is their relatively slow onset of effects. Of the four tear gas agents CS, CN (chloroacetophenone), CA (bromobenzyl cyanide), and CR (dibenzoxazephine), CS and CN appear to be the most widely used. Of these two CS is most widely used for training purposes. There are a number of reasons for this including both performance and safety characteristics:

- CS has a lower incapacitating threshold than CN, requiring less chemical to produce a similar response.

- A possible corollary to the above is a more rapid onset of CS effects compared to CN.

- CN has been reported to produce embryotoxicity in laboratory animals while CS has not (Elskamp, Upshall).

- Investigators (McNamara and Marrs et al.) have reported that chronic exposure to CS in laboratory animals does not increase risk of carcinogenesis/chronic toxicity. We are not aware of a similiar extensive body of research concerning CN.

- Studies on the acute inhalation toxicity of CN and CS indicate that CN is substantially more toxic than CS (Ballantyne and Swanston).

- As a corollary to the above difference in acute toxicities, there have been a number of human deaths reported from high-level acute CN exposures, while no deaths resulting from similar CS exposures have been reported.

- CN has more eye damaging potential than CS (Ballantyne, Gaskins).

- CN produces more severe acute contact dermatitis than CS (Ballantyne and Swanston)

- CN induced skin lesions heal more slowly than similar CS induced lesions (Ballantyne and Swanston).

A report by Beswick suggests that the more recently developed agent, Dibenzoxazepine (CR) may hold significant promise as a riot control agent. Table 1 lists the comparative properties of CN, CS, and CR. Comparison of high potency and low lethality would seem to indicate that CR is an effective agent. However, its alleged relative stability, a significant advantage for terrain denial purposes, may be a critical defect for training purposes, due to unacceptable accumulation in training areas. In any event, we are not aware of sufficient toxicity testing to determine CR safety for continuous use for training purposes.

Table 1
Comparison of CS, CN and CR

	CN	CS	CR
Eye irritation Threshold-aerosol(mg/m^3)	0.3	0.004	0.002
Aerosol Effective concentration mg/m^3	35	5	1
Estimated lethal dosage ($mg\ min/m^3$)	10×10^3	60×10^3	100×10^3

(Beswick)

III. CONCLUSIONS

A. Soil Degradation of CS

The breakdown of CS dispersed over soil from Eglin AFB under the controlled conditions of an environmental chamber was evaluated. The $t_{1/2}$ of CS under these conditions was 3.9 days. We believe this is a conservative estimate of the actual $t_{1/2}$ of CS under field conditions at Eglin. Depending on a variety of environmental factors that may increase the degradation of CS, the actual $t_{1/2}$ may vary, but most variation, except for cold climate and snow conditions, should be toward a shorter $t_{1/2}$. Thus the value 3.9 days can be used to conservatively estimate the extent of CS accumulation that will occur in soil from field exercises. (This value should not be used for CS which has been treated to extend its environmental persistence).

B. Analysis of Soil for CS

An analytical method for determining the amount of CS in soil was developed and validated. This method can be used to determine the actual levels of CS in soil at levels to 2 ppm.

C. Environmental Toxicity of CS

CS has been shown to be capable of producing toxicity in both terrestrial and aquatic plants and animals, including mammals. The hazard of CS contaminated soil will depend on the extent of contamination. Since CS does not accumulate within animals that consume it and degrades within the environment fairly quickly, a CS contaminated area will be, for practical purposes, CS-free (except for gross contamination) within weeks of the original dispersion. Continuous use of an area for CS dispersion can lead to a moderate accumulation of CS. For instance, dispersion of CS at 3 day

intervals will lead to an average soil burden of 2X the soil level resulting from the first CS dispersion. CS levels applied for terrain-denial purposes are intended to be acutely toxic to personnel. They should also have a similar toxicity for wildlife. These levels can also produce adverse effects in plants due to direct contact as well as decreasing germination. Aquatic species appear to be particularly sensitive to the effects of malononitrile, a CS breakdown product. However, the t½ of CS and degradation products in water is fairly short, so this appears to be a transient problem. CS levels utilized for training purposes, in general, are not harmful to the environment. However, areas proximate to a CS discharge may have CS contamination much higher than areas more distant from the discharge point. Concentrations in these limited areas may reach several hundred times the concentrations used in training and could potentially produce some limited adverse effects.

D. Alternative Agents for Training

A number of riot control agents have been used/recommended. Of these CS and CN are the predominant ones. From our evaluation of available safety information, CS appears to be more appropriate for training purposes.

IV. RECOMMENDATIONS

A. CS is an environmentally acceptable material for use in military training exercises when used in a prudent manner according to prescribed standards and regulations.

B. Local CS use may be restricted to certain sites or used in an undefined area. A method which meets local requirements should be selected. If large amounts of CS are frequently dispersed, we recommend that an area be identified for this purpose. You may wish to identify two or more areas, since rotational use of several sites will tend to reduce the CS burden at any one site. Infrequent use of small amounts of CS in remote areas normally should not require site restriction/identification. Continuous use sites should be selected to avoid direct drainage into areas where aquatic species may be exposed. Limiting CS dispersion at a site to 7 day intervals would clearly preclude any environmental buildup, while limiting dispersion to 3 day intervals could lead to a moderate environmental burden. In any event, a decision to "rest" a CS dispersion area for 30 days should result in a >99% decrease in soil CS burden.

C. The soil burden of CS may be determined by submitting soil samples to USAFOEHL. We do not recommend this be done routinely, but rather in rare circumstances when a requirement exists to identify or confirm areas of CS concentration which may pose a hazard, or to confirm a suspected exposure. When contemplating this analysis the short CS environmental t½ should be considered.

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Appendix A

Degradation of CS Applied to Soil from Eglin AFB

Table 2: CS Soil Depletion

Figure 2: CS Soil Depletion

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TABLE 2

CS DEPLETION IN SOIL

Sample Description[1] (Days)	% CS Remaining[2] (Mean ± Std Dev)
0.5	77 ± 8
1	73 ± 8
2	56 ± 10
4	51 ± 12
7	36 ± 3
10	15 ± 3
14	8 ± 2
28	0.6 ± 0.3
Darkness 2 (7) days[3]	78 ± 16 (65 ± 7)
Effects of Added H_2O[4] Mist (Rain)	35 ± 3 (35 ± 7)
Accumulation of CS from 5 soil spikes[5] Total CS Added: 50mg, Recovered: 27mg	54 ± 2
aerosolization of CS from soil[6]	
1 minute recovery from soil (bag)	98 ± 2 (1.9 ± 1.2)
4 day recovery from soil (bag)	22 ± 8 (trace)

[1] One gm of 1% CS in silica gel was applied to the surface of 50 gms of Eglin soil placed in a plastic dish.

[2] Each entry is mean of 5 replicates except 2 day entry where one replicate value was determined to be an outlying value and dropped.

[3] Dishes were covered with aluminum foil after CS was applied to soil. Sides of dishes were perforated to allow air circulation.

[4] with a spray bottle (.15 mL/pump). Mist exposure provided an application of .9 mL on days 1, 2, and 3, while rain exposed replicates received 9.0 mL on day 1. Analysis was done on day 4.

[5] CS was applied on alternate days 0-8 with analysis done on day 10.

[6] CS was applied to soil. Plastic dish was then placed inside a "zip loc" bag which was sealed. For analysis the dish was carefully removed from "zip loc" bag and the soil analyzed, while the inside surface of the bag was rinsed with methylene chloride which was then analyzed for CS.

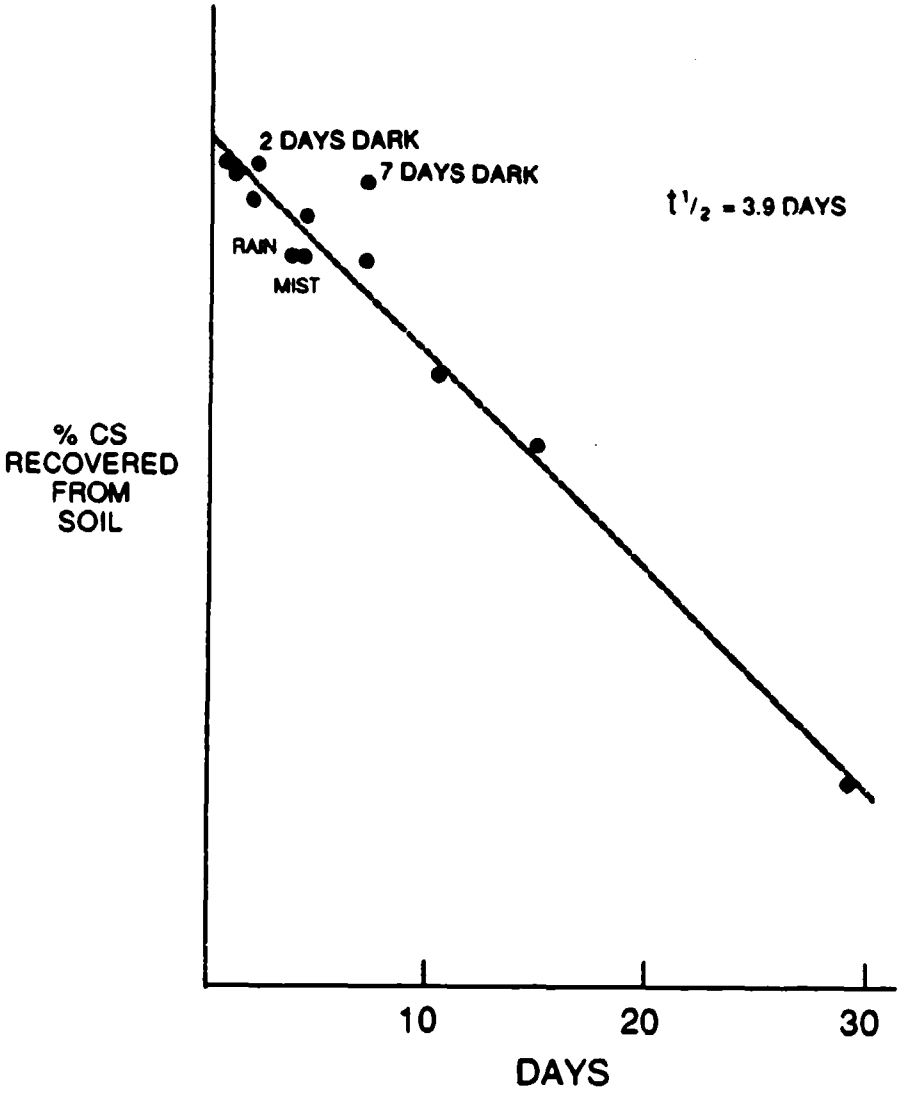

Figure 2 CS Soil Depletion

[1] A straight line approximation of the data was plotted using a semilog least-squares program based on the equation $A_o - A_e^{-kt}$ (Texas Instruments Statistics Manual, ST1).

[2] See previous table for description of parameters for individual data points.

Appendix B

Environmental Breakdown of CS

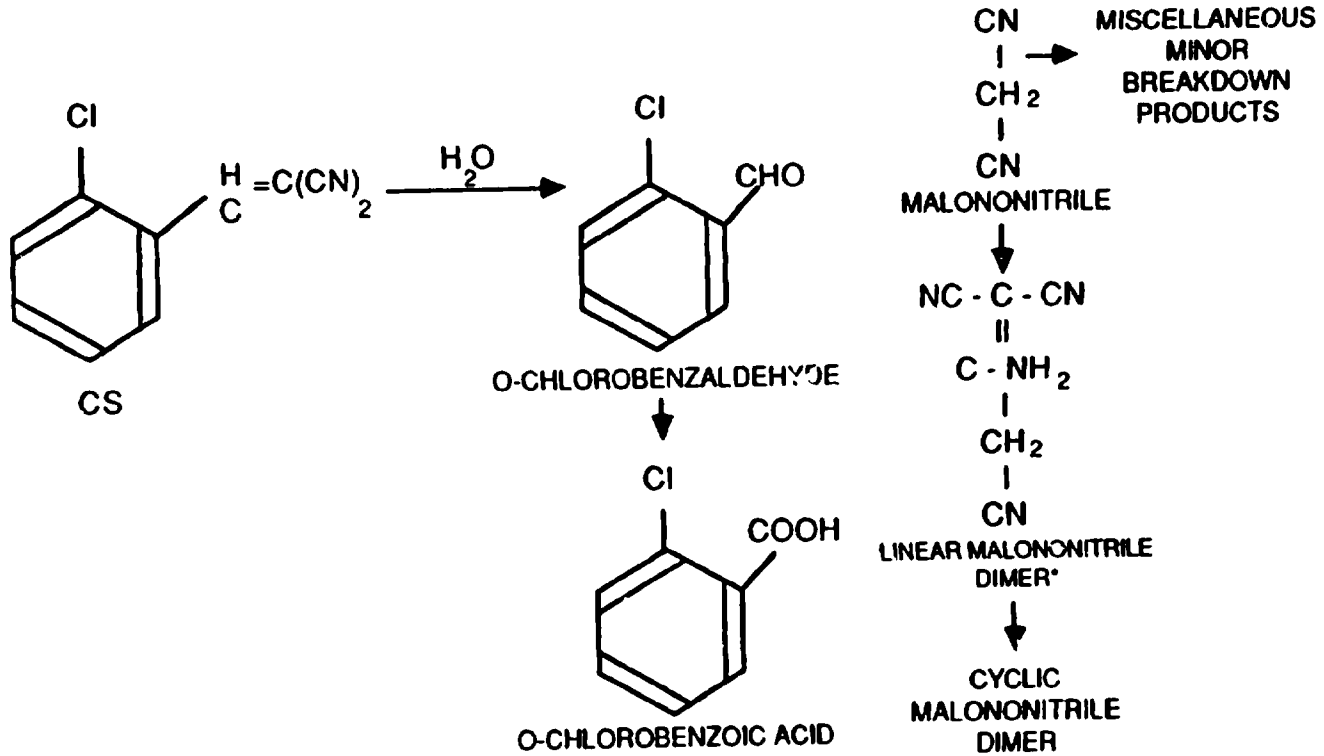

Figure 3: Major Hydrolysis Products of CS (Worthy and Schott)

*1,1,3-tricyano-2-amino-1-propene

Appendix C

Comprehensive CS Bibliography

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Appendix D

Alternate Riot Control Agents

TABLE 3

Alternate Riot Control Agents

Compound	Odor	Method of Dissemination	Onset	Signs and Symptoms	Recovery	Rx	Cutaneous Irritant Potential	Incapacitating Dose
CS	Pepperlike	Fine particulate aerosols	Few seconds at high concentrations	Ocular pain, Lacrimation, blepharospasm. Nasal irritation, rhinorrhea, sneezing. Coughing, mild dyspnea. Stinging of warm, moist skin. Conjunctivitis, Cutaneous burns (rare); allergic contact dermatitis.	Rapid (2-10 min)	None except for skin (see text)	0.5 mg/m^3 causes warm moist skin to sting	0.1-10 mg/m^3
CN	Apple blossoms	Fine particulate aerosols from pens, pistols, explosive cartridges	Rapid, but slower than CS	Same as CS except cough, dyspnea more prominent; headache, depression are late effects. Eye injuries from projectile dispensers. Conjunctivitis, burns.	Rapid (2-10 min)	Same as for CS	Moderate, less	22-220 mg/m^3
DM	Burning fireworks	Fine particulate smoke	Slow	Slight lacrimation, nasal irritation. Cough progressing to respiratory distress. Nausea and vomiting; headache, chills. Worsens after removal to fresh air.	Slow (20-30 min to days)	Chloroform inhalation for symptomatic relief of irritation	Weak, less than CS or CN	22-220 mg/m^3, but extremely variable
CA	Soured fruit	Liquid or vapor	Instantaneous	Irritates eyes and respiratory passages	Rapid (2-10 min)	None	Very little	30 mg/m^3
DC	Bitter almonds mixture	Fine particulate smoke	More rapid than DM	Like cold symptoms plus headache, vomiting, nausea	30 min to several hours, pending on concentrations	None	Very little	30 mg/m^3

(Sim)

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